1,2-DIBENZYLTETRADIMETHYLAMIDO-DIMOLYBDENUM AND -DITUNGSTEN (M≡M)

COMPOUNDS AND THEIR REACTIONS WITH CARBON DIOXIDE

AND 1,3-DIARYLTRIAZINES. A RADICAL DIFFERENCE.

by

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The preparation of 1,2-M_2(benzyl)$_2$(NMe$_2$)$_4$ ((M≡M)) compounds (M = Mo and W) and their reactions with each of CO_2 and 1,3-diaryltriazines are described. The molybdenum and tungsten dibenzyl compounds differ in their reactivity quite markedly. For tungsten, the M≡M bond is preserved in the formation of W_2(benzyl)$_2$-(NMe$_2$)$_2$(ArN$_3$Ar)$_2$ and W_2(benzyl)$_2$(O$_2$CNMe$_2$)$_4$ compounds, while molybdenum favors reductive elimination and formation of M-M quadruply bonded compounds Mo_2(O$_2$CN-Me$_2$)$_4$ and Mo_2(ArN$_3$Ar)$_2$, where Ar = phenyl and p-tolyl. Reductive elimination is shown to proceed via a radical pathway.

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1,2-Dibenzyltetradimethylamido-dimolybdenum and -Ditungsten (M≡M) Compounds and Their Reactions with Carbon Dioxide and 1,3-Diaryltriazines. A Radical Difference.

Sir:

Both molybdenum and tungsten have a rich dinuclear chemistry which in many ways, but by no means all ways, is very similar.[1] The search and ultimate discovery of a successful route to a tungsten $M_2(O_2CR)_4$ (M≡M) compound is an interesting story[2] and reveals what is now generally accepted: the $(W≡W)^{4+}$ unit is notably more reactive toward oxidative-addition reactions than the $(Mo≡Mo)^{4+}$ unit. McCarley's[3] spectacular success in preparing pure $MoW(O_2CBu^t)_4$ (M≡M) used this principle. We wish here to report an intriguing difference between reactions involving $(M≡M)^{6+}$ units (M = Mo and W)[4] which reveals the complementary fact: reductive elimination occurs for molybdenum, $(M≡M)^{6+} \rightarrow (M≡M)^{4+}$, but not for tungsten under comparable conditions.
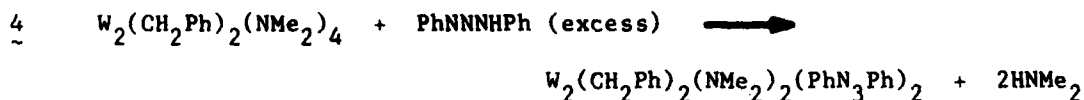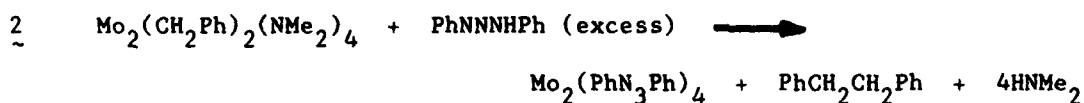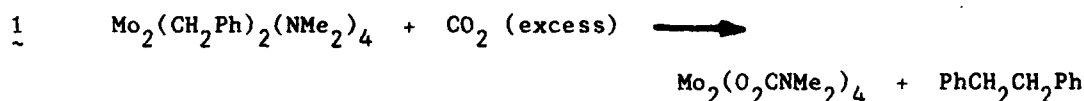
As part of a continuing study of the properties and reactions of $1,2-M_2R_2(NMe_2)_4$ (M≡M) compounds,[5] we have prepared $1,2-M_2(benzyl)_2(NMe_2)_4$ compounds (M = Mo, W) from reactions involving $1,2-M_2Cl_2(NMe_2)_4$ compounds[6] and benzyl-lithium or -Grignard reagents.[7] The new benzyl compounds are diamagnetic, air-sensitive, hydrocarbon soluble, yellow-orange crystalline solids. A gauche-$Mo_2(CH_2Ph)_2(NMe_2)_4$ molecule has been structurally characterized[8] and a view of the molecule is shown in Figure 1. The benzyl ligands are σ bonded and as a result of forming a Mo≡Mo bond, three Mo-L σ bonds and two Me_2N-to-Mo π bonds, each metal atom attains a 16 valence shell of electrons. The benzyl compounds are thus directly

analogous to 1,2-$M_2R_2(NMe_2)_4$ compounds recently reported[5] for M = Mo and W and R = Me, Et, n-, and i-Pr and n-, s- and t-Bu, and in solution they exist in both anti and gauche rotamers.

The molybdenum and tungsten compounds differ in their reactions[9] with CO_2 and 1,3-diaryltriazines as shown in reactions 1-4.

1     $Mo_2(CH_2Ph)_2(NMe_2)_4$ + CO_2 (excess) $\longrightarrow$

$$Mo_2(O_2CNMe_2)_4 + PhCH_2CH_2Ph$$

2     $Mo_2(CH_2Ph)_2(NMe_2)_4$ + PhNNNHPh (excess) $\longrightarrow$

$$Mo_2(PhN_3Ph)_4 + PhCH_2CH_2Ph + 4HNMe_2$$

3     $W_2(CH_2Ph)_2(NMe_2)_4$ + CO_2 (excess) $\longrightarrow$ $W_2(CH_2Ph)_2(O_2CNMe_2)_4$

4     $W_2(CH_2Ph)_2(NMe_2)_4$ + PhNNNHPh (excess) $\longrightarrow$

$$W_2(CH_2Ph)_2(NMe_2)_2(PhN_3Ph)_2 + 2HNMe_2$$

The tungsten compounds $W_2(CH_2Ph)_2(O_2CNMe_2)_4$ and $W_2(CH_2Ph)_2(NMe_2)_2$-$(PhN_3Ph)_2$ are spectroscopically analogous to compounds which have been characterized by single crystal X-ray studies: $W_2Me_2(O_2CNMe_2)_4$ (M≡M)[10] and $Mo_2Me_2(NMe_2)_2(PhN_3Ph)_2$ (M≡M).[11] There can be little, if any, doubt that the (W≡W)$^{6+}$ unit is retained in the benzyl derivatives formed in reactions 3 and 4. The existence of the (Mo≡Mo)$^{4+}$ unit in the compounds $Mo_2(O_2CNMe_2)_4$ and $Mo_2(ArN_3Ar)_4$ is similarly certain and has been established by single crystal X-ray studies for Ar = phenyl[12] and p-tolyl.[13]

The transformation of the $(M \equiv M)^{6+}$ unit to $(M \equiv M)^{4+}$ which occurs for molybdenum, but not for tungsten, has a parallel in the reactions of $1,2-M_2R_2(NMe_2)_4$ compounds with each of CO_2 and 1,3-diaryltriazines, where R = Et, Pr and Bu.[13,14] See eq. 5.

5    $Mo_2R_2(NMe_2)_4 + CO_2$ (excess)   ➞

$$Mo_2(O_2CNMe_2)_4 + \text{alkene} + \text{alkane}$$
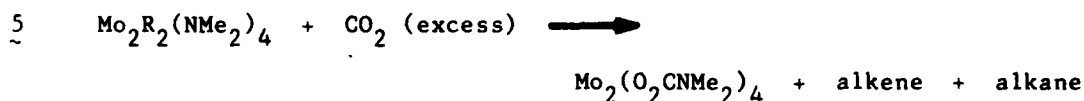
In reaction 5, alkyl group disproportionation is intramolecular and involves the transference of a β-hydrogen of one alkyl ligand to the α-carbon of the other: $M_2(CH_2CD_3)_2 \rightarrow M_2 + CH_2=CD_2 + CH_2DCD_3$. When R = CH_3 and CH_2SiMe_3, no reductive elimination occurs and $Mo_2R_2(O_2CNMe_2)_4$ compounds are obtained.[13]

A number of observations suggest that the formation of dibenzyl in eq. 1 occurs by a radical pathway. (1) Reactions involving 1:1 mixtures of $Mo_2(CH_2Ph)_2(NMe_2)_4$ and $Mo_2(CH_2-p-tolyl)_2(NMe_2)_4$ with CO_2 in hexane or benzene give a statistical mixture of coupled products: $PhCH_2CH_2Ph$, $PhCH_2CH_2-p-tolyl$, and $p-tolyl-CH_2CH_2-p-tolyl$ which were characterized by g.c.,[15] g.c.-m.s. and high field ^{1}H nmr spectroscopy. (2) In addition to dibenzyl, some toluene (or xylene) was always formed and when reaction 1 was carried out in the presence of 1,4-cyclohexadiene, toluene (or xylene) was produced with concommitant suppression of dibenzyl (or $p-tolyl-CH_2CH_2-p-tolyl$). (3) Attempts to trap benzyl radicals during the course of 1 using nitrosodurene as a radical trap were thwarted by the fact that, in hexane, nitrosodurene and $Mo_2(CH_2Ph)_2(NMe_2)_4$ react, yielding the characteristic esr signal of the trapped benzyl radical and as yet uncharacterized molybdenum containing products.[16]

If one accepts the above as evidence for a radical elimination pathway, then tungsten by favoring the higher oxidation state should be less willing (than molybdenum) to undergo metal-carbon (alkyl) bond homolysis which would result in an oxidation state change from 3 to 2.[17] Analogous reasoning has been used in cobalt-carbon chemistry where it has been shown that ligand basicity affects $D_{(Co-R)}$. The more basic the ligand, the larger the value of $D_{(Co-R)}$ which is attributed to the stabilizing effect on the higher oxidation state, Co(III) relative to Co(II), the latter being formed upon homolysis of the Co-alkyl bond.[18] In view of the similar values obtained[19] for $D_{(Co-R)}$ in organocobalt Schiff base compounds [py(saloph)Co-R], where py = pyridine and saloph = N,N'-bis(salicylidene)-o-phenylenediamine and R = alkyl (n- and i-Pr) and benzyl, it is possible and even quite probable that a radical mechanism could be involved in 5. Alkyl group disproportionation could occur by β-hydrogen abstraction within the solvent cage of the geminate dimolybdenum-alkyl radical pair formed upon homolysis of one of the Mo-C (alkyl) bonds. Further studies aimed at extracting mechanistic information are planned.[20]

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References

1. Cotton, F.A.; Walton, R.A. in "Multiple Bonds Between Metal Atoms", John Wiley & Sons, Publisher, 1982.

2. Sattelberger, A.P.; McLaughlin, K.W.; Huffman, J.C. J. Am. Chem. Soc. 1981, 103, 2880 and references therein.

3. From the reaction among $Mo(CO)_6$, $W(CO)_6$ and Bu^tCOOH, mixtures of $Mo_2(O_2CBu^t)_4$ and $MoW(O_2CBu^t)_4$ were obtained. Addition of I_2 to a benzene solution of a mixture of these Mo_2- and MoW-containing compounds selectively precipitated the heterobimetallic single electron oxidation product $MoW(O_2CBu^t)_4I$, and a crystal structure of the acetonitrile adduct revealed axial coordination of I^- to W and MeCN to Mo. The compound has a bond order of 3.5 and reduction, using powdered zinc in acetonitrile at $25^{\circ}C$, yielded the heterobimetallic quadruply bonded compound $MoW(O_2CBu^t)_4$. Katovic, V.; Templeton, J.L.; Hoxmeier, R.J.; McCarley, R.E. J. Am. Chem. Soc. 1975, 97, 5300.

4. Chisholm, M.H.; Cotton, F.A. Acc. Chem. Res. 1978, 11, 356.

5. Chisholm, M.H.; Haitko, D.A.; Folting, K.; Huffman, J.C. J. Am. Chem. Soc. 1981, 103, 4046.

6. Akiyama, M.; Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Murillo, C.A. Inorg. Chem. 1977, 16, 2407.

7. All reactions were carried out using dry and oxygen-free solvents and atmospheres. Satisfactory analytical data were obtained.

8. Crystal data at $-165^{\circ}C$: $a = 17.595(7)$ Å, $b = 16.038(6)$ Å, $c = 10.542(4)$ Å, $\beta = 122.11(2)^{\circ}$, $Z = 4$ and $d_{calcd} = 1.451$ g cm^{-3} in the space group $P2_1/a$. Of the 5121 reflections collected, the 3916 having $F >$

2.33 $\sigma(F)$ were used in the full matrix refinement. Final residuals are
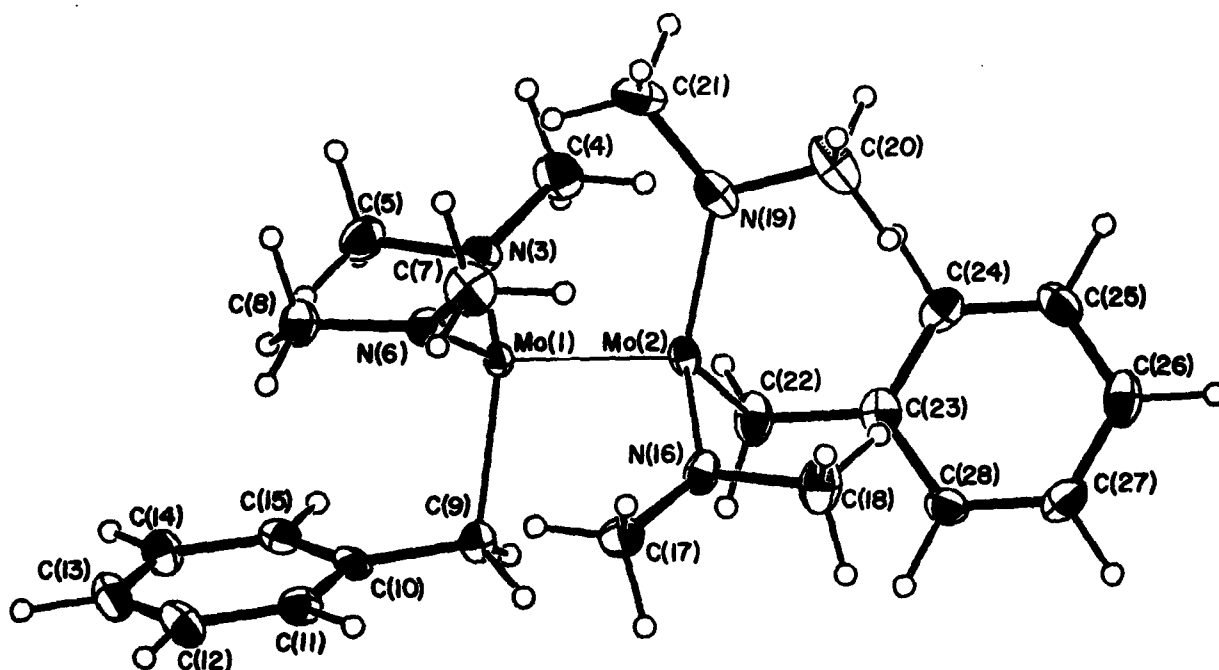R(F) = 0.036 and Rw(F) = 0.037.

9. Reactions were carried out in hexane or benzene at room temperature
in a manner previously described: ref. 13.

10. Chisholm, M.H.; Cotton, F.A.; Extine, M.W.; Stults, B.R. Inorg. Chem.
1977, 16, 603.

11. Chisholm, M.H.; Haitko, D.A.; Huffman, J.C. Inorg. Chem. 1981, 20,
2211.

12. Cotton, F.A.; Rice, G.W.; Sekutowski, J.C. Inorg. Chem. 1979, 18,
1143.

13. Chetcuti, M.J.; Chisholm, M.H.; Folting, K.; Haitko, D.A.; Huffman,
J.C. J. Am. Chem. Soc. 1982, 104, 2138.

14. Chisholm, M.H.; Haitko, D.A. J. Am. Chem. Soc. 1979, 101, 6784.

15. We thank Dr. Kevin Gilbert for assistance in obtaining g.c. analyti-
cal data.

16. We thank Dr. Willie Lau for assistance in obtaining esr results.

17. An alternate, but essentially similar argument can be made on the
observed general trends for $\overline{D}(M-L)$ in homoleptic transition metal
complexes. "In general the mean bond enthalpy, $\overline{D}(M-L)$ decreases in
the order of L = F > OR > Cl > NR_2 > CH_2R and the values increase
monotonically from one transition series to another in the order
M(3d) < M(4d) < M(5d)... The mean bond enthalpy $D(M-CH_2R)$ increases
with increasing atomic number in any one group whereas in the main
group (s, p-block) metals the mean bond enthalpy decreases in the
same sense." Connor, J.A. Topics in Current Chemistry 1977, 71, pp.
83-84.

18. Ng, F.T.T.; Rempel, G.L.; Halpern, J. J. Am. Chem. Soc. 1982, 104, 621.

19. Tsou, T.T.; Loots, M.; Halpern, J. J. Am. Chem. Soc. 1982, 104, 623.

20. We thank the Office of Naval Research and the Petroleum Research Fund administered by the American Chemical Society for support.

Caption to Figure

An ORTEP view of the gauche-1,2-Mo_2(benzyl)$_2$(NMe$_2$)$_4$ molecule. Some pertinent bond distances ($\overset{o}{A}$) and bond angles (degrees) (averaged where appropriate) are Mo-Mo = 2.200(1), Mo-N = 1.950(5), Mo-C = 2.19(1), Mo-Mo-N = 104(1)^{o}, Mo-Mo-C = 100.0(4)^{o}. The Mo-to-orthocarbon distances are essentially all the same at 3.7 $\overset{o}{A}$.

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